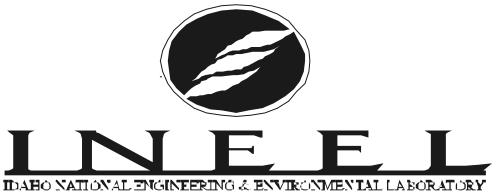
INEEL/CON-99-01155
PREPRINT



A Novel Synthesis of Polyesters Containing Hexa-(tert-butylhydroquinone)cyclotriphosphazene

F. F. Stewart
T. A. Luther
M. K. Harrup
R. P. Lash

March 26, 2000 – March 30, 2000

National American Chemical Society Meeting

BECHTEL BWXT IDAHO, LLC

A Novel Synthesis of Polyesters Containing Hexa-(*tert*-butylhydroquinone)cyclotriphosphazene

Frederick F. Stewart, Thomas A. Luther, Mason K. Harrup, Robert P. Lash

Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208

Introduction

The majority of polyphosphazene material research has concentrated on the linear polymer configuration.[1] However, this represents only one of three potential backbone configurations for phosphazenes, see Figure 1. Linear polymers are formed either directly from phosphorus and nitrogen containing precursors[2] or from the ring opening polymerization of hexachlorocyclotriphosphazene.[3] Two other backbone structures can be formed from hexachlorocyclotriphosphazene: cyclolinear and cyclomatrix. Cyclolinear are the least studied due to synthetic difficulty. Cyclomatrix polymers represent a more facile method for forming non-linear phosphazenes.[4]

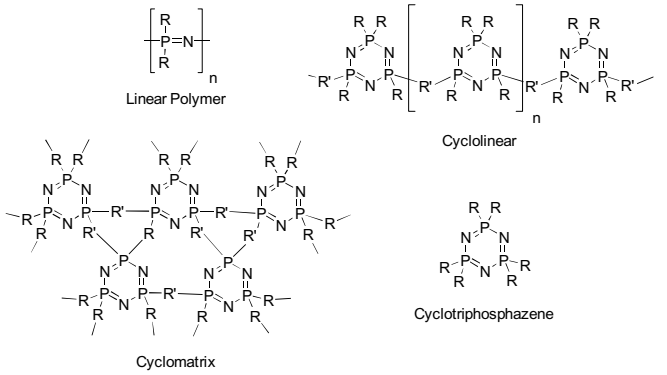


Figure 1. Polyphosphazene Backbone Configurations. R and R′ represent monodentate pendant groups and bidentate crosslinking groups, respectively.

Interest in cyclomatrix phosphazenes is driven by the desire to reduce material cost while taking advantage of the inherent stability of the inorganic phosphazene backbone. In an earlier report,[5] the synthesis of hexa-(*tert*-butylhydroquinone)cyclotriphosphazene (tbuHQCP) was described (Figure 2). This cyclotriphosphazene was formed with regiospecificity with the *tert*-butyl group positioned away from the inorganic ring. Additionally, this cyclotriphosphazene exhibited no oligomerization due to reaction with both hydroxyls of *tert*-butylhydroquinone, as opposed to syntheses reported using simple hydroquinone.[6]

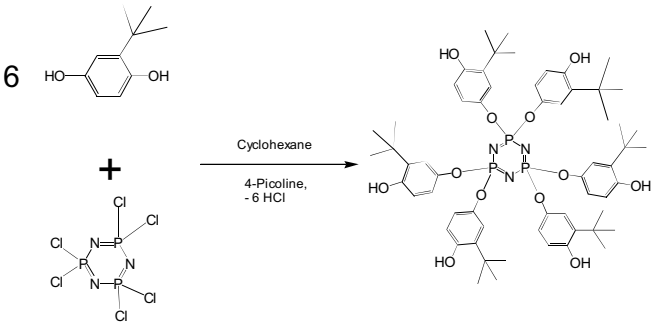


Figure 2. Synthesis of Hexa-(*tert*-butylhydroquinone)cyclotriphosphazene.

Experimental Section

All NMR spectra were acquired using a Bruker AC-300P or a Bruker DMX-300WB spectrometer operating at 300.1 MHz (^{1}H), 75.5 MHz (^{13}C) and 121.5 MHz (^{31}P). Proton NMR spectra were referenced to the tetramethylsilane (TMS) (0.00 ppm) (Cambridge Isotopes). All ^{13}C spectra were referenced to TMS at 0.0 ppm. All ^{31}P spectra were referenced to an external H_3PO_4. Glass transition temperatures were determined using a TA Instruments model 2910 differential scanning calorimeter and TGA analyses were performed using a TA Instruments Model 2950 Thermogravimetric Analyzer. High Performance Size Exclusion Chromatography and Detection (HPSEC) was performed using a Waters Model 2690 solvent/sample delivery system with a column bank of two Styragel HR 5E (4.6 mm id. x 300 mm) solvent-efficient columns. The polymers were detected using the Wyatt Technologies Dawn-DSP laser light scattering (LLS) detector with the F2 flow cell that measures scattered light intensities at 16 angles ranging from 12.3° to 165.1°.

Reaction of tbuHQCP with Acetic Anhydride to yield Hexa-((4-acetyl)(3-*tert*-butyl)phenoxy)cyclotriphosphazene. A 50 mL flask was charged with 1.0g (0.89 mmol) of tbuHQCP, 15 mL of dry 1,4-dioxane, and 550 μL (5.8 mmol) of acetic anhydride. To this was added 544 μL (5.6 mmol) of 4-picoline followed by stirring at ambient temperature for 15 hours. The mixture was heated to reflux for 6 hours and then cooled. Isolation was accomplished by adding CH_2Cl_2 to the reaction mixture in a separatory funnel and washing the organic fraction with three portions of water, three portions of dilute HCl, and three portions of dilute $NaHCO_3$. The CH_2Cl_2 was stripped off by rotary evaporation to yield a pale pink solid in 74% yield. ^{31}P NMR (acetone-d_6) δ 9.90 ppm. ^{13}C NMR (acetone-d_6) δ 169.4, 148.4, 147.0, 143.3, 126.1, 119.3, 117.2, 35.0, 30.0, 21.4. ^{1}H NMR (acetone-d_6) δ 7.27, 7.03, 6.84, 2.38, 1.34. DSC T_m 65 °C.

Reaction of tbuHQCP with Adipoyl Chloride to yield Polymer 1. To a 25 mL flask was added a magnetic stirrer, 1.0 g (0.89 mmol) of tbuHQCP and 10 mL of dry 1,4-dioxane. A condenser with an addition adapter was added and the apparatus was sealed with septa and flushed with dry nitrogen. To this, 3.87 mL (27 mmol) of adipoyl chloride was added by syringe and the resulting mixture was heated to reflux for 6 hours. After cooling, the resulting mixture was added to a separatory funnel containing 50 mL of water. The aqueous solution was extracted with three 50 mL portions of diethyl ether. The organic phases were collected and the diethyl ether was stripped using a rotary evaporator to yield a brown solid, polymer **1** in 27% yield. Polymer **1**: ^{31}P NMR (acetone-d_6) δ 9.90. ^{13}C NMR (acetone-d_6) δ 174.0, 171.3, 147.4, 146.1, 142.4, 125.2, 119.1, 118.4, 66.5, 65.1, 34.1, 32.9, 27.0. Dilute Solution LLS M_w (3.3±1.0) x 10^5, RMS Radius 152.0 ± 37.5 nm, dn/dc = 0.121 mL/g.

Reaction of tbuHQCP with Succinyl Chloride to yield Polymer 2. To a dry 50 mL flask was added 2.0 g (1.78 mmol) of tbuHQCP, 30 mL of dry 1,4-dioxane, and a magnetic stirrer. An addition adapter and a condenser were added to the apparatus followed by septa and nitrogen purge. Succinyl chloride (5.9 mL, 53.5 mmol) was added by syringe and the resulting mixture was heated to reflux for 48 hrs upon which the reaction was quenched with water and Polymer **2** was isolated by extraction with CH_2Cl_2. Stripping of the CH_2Cl_2 gave a tan colored solid that was then extracted using hot water in a soxhlet extractor to give 0.7 g of Polymer **2** (51% yield). Polymer **2**: ^{31}P NMR (acetone-d_6) δ 9.95. ^{13}C NMR (acetone-d_6) δ 173.2, 171.2, 148.1, 146.5, 142.9, 125.4, 119.6, 118.8, 34.6, 28.5. HPSEC-LLS M_w (3.46±0.03) x 10^5, RMS radius 73.4±0.7, polydispersity (M_w/M_n) 1.39±0.02.

Reaction of tbuHQCP with Dodecanedioyl Dichloride to yield Polymers 3 and 4. Polymers **3** and **4** were synthesized using a similar method. Polymer **3** was synthesized with a ratio of acid chloride/aromatic hydroxyl on phosphazene at 3.5:1 where Polymer **4**, a ratio of 2.0:1. The representative synthesis of Polymer **3** is included here. To a 100 mL flask was added 5.5 g (4.9 mmol) of tbuHQCP, 50 mL of dry 1,4-dioxane, a magnetic stirrer, an addition adapter, and a condenser. The system was sealed with septa and purged with dry nitrogen. To this apparatus was added by syringe 12.9 mL (52 mmol) of dodecanedioyl dichloride and the resulting mixture was heated for 22 hours and then allowed to cool. The reaction was quenched with 1 L water and the insoluble solids were collected by centrifugation. These solids were then treated with 100 mL of diethyl ether and centrifuged to remove insoluble material. The solution was collected by decantation and polymer **3** was isolated by stripping the etherial solution to give 6.9 g (60%) of a tan solid. Polymer **3** and **4**: ^{31}P NMR (acetone-d_6) δ 10.0. ^{13}C NMR (acetone-d_6) δ 174.9, 172.0, 148.2, 146.9, 143.1, 125.9, 119.9, 119.2, 34.9, 34.0, 25.3. Polymer **3**: HPSEC LLS M_w (1.39±0.6) x 10^6, RMS radius 103.9±24.9 nm, polydispersity (M_w/M_n) 1.99. Polymer **4**: HPSEC LLS M_w (1.22±0.5) x 10^6, RMS Radius 103.4±20.9 nm, polydispersity (M_w/M_n) 3.03.

Results and Discussion

As a probe of the reactivity of the free hydroxyl, tbuHQCP was reacted with acetic anhydride in the presence of base to give the fully acetylated hexa-

((4-acetyl)(3-*tert*-butyl)phenoxy)cyclotriphosphazene. Characterization of this new phosphazene was accomplished using ^{13}C NMR spectroscopy. Three resonances, see Figure 3, were noted for tbuHQCP that correspond to the protonated aromatic carbons: 116.0, 118.1, and 119.0 ppm. For the acetylated product, the protonated aromatic carbons were measured at 117.2, 119.3, and 126.1 ppm. Additionally, the expected carbonyl resonance was located at 169.4 ppm.

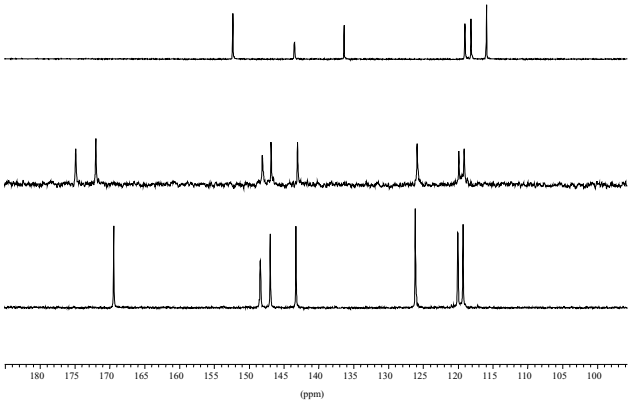


Figure 3. ^{13}C NMR spectra of the aromatic region for tbuHQCP (top), acetylated tbuHQCP (bottom), and polymer **3** (middle). The spectra were collected at room temperature in acetone-d_6 as solvent.

Given the reactivity of tbuHQCP towards an acid anhydride, it was proposed that polymerized products could be obtained using bifunctional organic linkers such as diacid chlorides. Reaction between a hydroxylated cyclotriphosphazene and a diacid chloride would yield a hybrid inorganic-organic polyester polymer.

Reactions were conducted in THF with a three-fold excess of adipoyl chloride under refluxing conditions and were monitored by ^{13}C NMR spectroscopy. The aromatic region showed the same fingerprint as the acetylation reactions but the aliphatic region was dominated by six large peaks that could not be attributed to either the adipoyl chloride or tbuHQCP. Upon vacuum distillation of the reaction residue after removal of THF, a copious amount of a high boiling clear viscous oil was isolated that corresponded to the six aliphatic NMR signals. Characterization revealed the oil to be an adipoyl chloride adduct to THF where the ring has been opened. Ring opening of THF was a curious side product of this synthetic reaction. This is not a new phenomenon. Cleavage of ethers by acid chlorides with cobalt (II) catalysis has been studied.[7] Without a rigorous investigation, it is not possible to propose a detailed mechanism except to assert that the cyclotriphosphazene may act as a catalyst for the formation of the THF adduct.

To eliminate the unwanted side product, THF was replaced with 1,4-dioxane. In this solvent, polymer **1** was synthesized as a brown glass-like solid. Laser Light-Scattering (LLS) was employed to determine the M_w, measured at 330,000 g/mol suggesting a high degree of bidentate linkages between cyclotriphosphazene rings. The M_w represents approximately 267 mers per average chain. Thermal analysis of this new polymer showed only a melt endotherm, see Table 1. The most notable nature of this new polymer is the high degree of solubility in organic solvents, a property that is not common for cyclomatrix phosphazenes.

High levels of solubility allowed for liquid state ^{13}C NMR analysis. The protonated aromatic carbons were observed to shift consistent with acetylated product. Surprisingly, two peaks at 174.0 ppm and 171.3 ppm were noted. From analogy to the acetylation reactions, the peak at 171.3 ppm was assigned to the ester carbonyl and the peak at 174.0 ppm was assigned to an acid carbonyl. The data suggest that attachment of adipic ester moiety may occur either in a bidentate pathway giving a crosslink between two cyclotriphosphazene rings or in a monodentate fashion where only one end of the diacid chloride attaches to the phosphazene. The free end is subsequently hydrolyzed during product purification.

Succinyl dichloride was employed to provide a longer carbon bridge between phosphazene rings. The reaction time in this instance was substantially longer, at 48 hours, and polymer **2** was isolated as a tan colored brittle glassy solid. Thermal analysis indicated a similar melt endotherm to the adipic polymer. ^{13}C NMR spectra data showed the same general trend with three peaks for the protonated aromatic carbons and two peaks in the carbonyl region. Molecular weight characterization of this polymer was accomplished through High Performance Size Exclusion Chromatography (HPSEC) with Laser Light Scattering (LLS) detection. The degree of polymerization was similar that of polymer **1** with approximately 287 mers per chain.

Table 1. Thermal Analysis Data for Polymers 1-4 .

Polymer	T_g (°C)	T_l (°C)	T_m (°C)	T_d (°C)
1	None observed	61	None observed	161
2	None observed	71	None observed	207
3	14	53	115	207
4	21	56	116	201

Reaction with dodecanedioyl dichloride was observed to give waxy polymeric products. These polymerizations were performed at three different stoichiometries to investigate the dependence of synthetic process on molecular weight. Ratios of diacid chloride to aromatic hydroxyl studied included 1:1, 2.0:1, and 3.5:1. At a ratio of 1:1, the reaction solution solidified during reflux forming a 1,4-dioxane-swollen gel. Attempts to isolate soluble polymer through removal of the solvent under reduced pressure followed by dissolution in other solvents were performed without success. It is proposed that the material was highly crosslinked. To control the amount of bidentate reactivity, an excess of diacid chloride was employed with success. At ratios of 2.0:1 and 3.5:1, soluble polymers were isolated and characterized. Figure 3 contains a plot of the aromatic and carbonyl region for polymer **3** that illustrates the significant resonances in the ^{13}C NMR spectra, including both carbonyl peaks. Molecular weights (M_w) for these species were similar and confirmed the polymeric nature of the products.

Thermal analytical data of polymers **3** and **4** were similar to each other, as expected. The significant difference between the polymer data observed for the shorter chain systems and for polymers **3** and **4** was a measurable T_g. The T_g for polymers **3** and **4** was 14 °C and 21 °C, respectively, suggesting that these polymers have an amorphous component to them. Additionally, two endotherms were observed. Decomposition (T_d) for both of these polymers was measured in excess of 200 °C.

Conclusion

Novel organic-inorganic hybrid polymers were synthesized and characterized. These materials were fully soluble in common solvents such as acetone and tetrahydrofuran. The methodology employed was an ester coupling with varying length organic spacers between inorganic cyclotriphosphazene rings. The shorter spacer chain lengths, four and six carbons, gave polymers that were highly glassy and did not exhibit a glass transition temperature in the range of -150 °C to +220 °C. Twelve carbon chain length spacers gave waxy materials with observable glass transitions. Thermal stabilities of these materials ranged from 161 °C to 207 °C, considerably lower than many linear phosphazenes, suggesting that the organic component of the backbone is responsible for this lower stability. The soluble nature of these polymers will allow for their use as thin films in applications such as membranes.

Acknowledgement

The work described in this paper was supported by the United States Department of Energy through Contract DE-AC07-99ID13727.

References

[1] Mark, J.E.; Allcock, H.R.; West, R., *Inorganic Polymers*, Prentice Hall, Englewood, NJ, 1992, pp. 61-140.
[2] Stokes, H.N. *Amer. Chem. J.,* **1895**, *17*, 275.
[3] Allcock, H.R.; Kugel, R.L. *J. Am. Chem. Soc.* **1965,** *87*, 4216.
[4] DeJaeger, R; Gleria, M *Prog Polym. Sci.* **1998**, *23*, 179.
[5] Stewart, F.F. Harrup, M.K. *J. Appl. Polym. Sci.***1999**, *72*, 1085.
[6] Femec, D.A.; McCaffrey, R.R. *J. Appl. Poly. Sci.* **1994,** *52*, 501.
[7] Ahmad, S.; Iqbal, J. *Chem. Lett.* **1987**, 953.